

# A CONTRIBUTION TO THE STUDY OF THE STABILITY OF CLAY MINERALS FROM THE SOIL SOLUTION COMPOSITION AT DIFFERENT pF VALUES

M. L. FERNANDEZ-MARCOS, F. MACIAS, F. GUITIAN-OJEA

Cátedra de Edafología, Facultad de Farmacia, Santiago de Compostela, Spain

**ABSTRACT:** The composition of the soil solution of various horizons of Galician soils was studied to gain insight into the direction of the processes of weathering and neoformation by means of stability diagrams of the clay minerals. The soil solution was extracted by compression at various pF values.

The most significant results are as follows: In all the cases studied the mineral in equilibrium with the soil solution is a 1:1 phyllosilicate. As the pF at which the soil solution is extracted increases, corresponding to smaller pore size, pH increases and silica concentration falls. The stable mineral does not vary significantly between different horizons of the same profile. Each parent material gives rise to a different zonation in the stability diagrams. The predictions of the stability diagrams are in general agreement with the mineralogical data of the clays of the horizons in question.

Finally, weathering processes in Galicia are briefly commented on.

The use of water composition data in mineral stability studies is a method frequently employed in recent years, especially since Garrels & Christ (1965), Kittrick (1969) and other authors expressed their ideas on the relationship between the soil solution and the present and future mineralogical composition of the soil.

The validity of the method has been the subject of some controversy, since it may be supposed that an open system such as the soil never reaches equilibrium conditions, but rather a steady state (Johnson, 1971). Equilibrium concepts would thus only be applicable if the reaction rate and residence time were large enough, conditions which are obviously not satisfied in all cases.

In spite of this limitation, there is no doubt that the method may give a valid indication of the general tendencies of weathering and neoformation. It has been used in this way by several researchers: Feth et al. (1964) and Sutherland (1970) use data from ephemeral and perennial springs; Tardy (1971), Garcia Sanchez & Saavedra (1975) and Garcia Paz et al. (1977) from rivers and streams; Upchurch et al. (1973) and Grandal et al. (1976) from lysimetric waters, etc.

However, spring water, the water of rivers and streams, and lysimetric waters cannot be expected to be in equilibrium with the minerals of the clay fraction of the soil. If equilibrium is attained at all, it will be between these minerals and the soil solution of each horizon and it cannot be assumed *a priori* that the water of rivers, streams or springs, or lysimetric waters, accurately reflect the composition of the soil solution. Various researchers have discovered empirically significant differences between the composition of lysimetric waters and that of the corresponding soil solutions (Shilova et al., 1961, 1962, 1963; Samoylova & Demkin, 1976). These differences are readily understood when one remembers that lysimetric water is fundamentally gravitational water which filters rapidly and which consequently interacts much more weakly with the solid phase. All the more reason, therefore, to expect differences between the composition of the soil solution and that of spring, river or stream water (Birkeland, 1974).

For these reasons it would be more appropriate to use the soil solution itself for the study of mineral stability by means of stability diagrams. An example of such a study is the recent work of Wilke & Schwertmann (1977) in which the soil solution is used to determine whether the gibbsite present in a profile is stable or not under present conditions.

The aims of the present authors were: (1) to study mineral stability using the soil solution extracted by compression at various pF values from different soil horizons; and (2) to compare the information so obtained with that derived from the study of stream water flowing over the same parent material and with the data now available on the mineralogy of the fine fraction of Galician soils.

## MATERIAL AND METHODS

Samples were collected from eight profiles of Galician soils over a variety of parent materials: gabbros, amphibolites, mica-schists and granites. In Table 1 the main characteristics of the horizons studied are indicated.

TABLE 1. Chief characteristics of the horizons studied

Profile no.	Diagnostic Horizon FAO (1973)	pH (H <sub>2</sub> O)	pH (KCl 0.1 M)	Org. matter (%)	Clay (%)	Type of clay present
Gabbros*						
1328	A umbric (Aul)	5.10	4.40	21.95	36.1	metahalloysite, amorphous Al
1328	A umbric (Au2)	4.80	4.60	14.17	32.6	metahalloysite, amorphous Al
1328	B cambic (2B)	4.80	3.90	0.91	47.9	kaolinite, gibbsite
1330	A umbric (Aul)	5.20	4.40	18.48	39.9	metahalloysite, amorphous Al
1330	A umbric (Au2)	5.10	4.40	13.38	30.7	amorphous Al, metahalloysite
Amphibolites†						
677	A umbric (A)	5.25	4.70	19.60	31.0	chlorite, kaolinite
677	B cambic (2B)	5.10	4.20	0.38	22.0	kaolinite, goethite
1271	A umbric (A)	5.30	4.50	15.17	22.0	chlorite, kaolinite
1271	B cambic (2B)	5.20	4.20	1.21	25.0	kaolinite
Schists						
1433	A umbric (Aul)	5.10	4.10	12.05	14.6	kaolinite, illite
1433	A umbric (Au3)	5.75	4.10	10.79	13.2	kaolinite, illite
1449	A umbric (A)	5.45	4.60	3.76	9.8	kaolinite, illite
1449	B cambic (B2)	5.90	4.60	0.95	16.5	kaolinite
1449	B cambic (B3)	5.40	4.40	0.50	9.2	kaolinite
Granites†						
1284	A umbric (A)	4.50	3.90	11.22	8.5	illite, vermiculite
1233	A umbric (A)	4.60	3.90	10.26	7.5	vermiculite, illite
1233	A umbric (2A)	4.90	4.20	11.83	9.5	vermiculite, illite

\* The A horizons have a high percentage of amorphous material and the B horizons show ferrallic properties. The general data on these profiles are to be found in the papers of Macías et al. (1977).

† The data on this profiles are to be found in Actas del I Congreso de Suelos de Galicia, NW España (Guitián et al., 1973).

The samples, collected at field capacity humidity conditions ( $pF \approx 2.5$ ), were subjected to extraction of the soil solution by compression at  $pF$  3.0, 3.5 and 4.2, using the Richards (1941) cell. In some horizons Ishcherekov's (1907) method of displacing the solution with ethanol was used, but this procedure was discarded owing to the discrepancy between the results so obtained and those obtained by the compression method.

The following determinations were carried out on the solutions: pH; Ca, Mg, Na and K by atomic absorption spectroscopy; Si by spectrophotometry of the silico-molybdic

blue complex and Al by spectrophotometry with aluminon as chromogenic agent (Guitian & Carballas, 1976).

## RESULTS AND DISCUSSION

The data obtained from the analysis of the soil solution at different pF values are given in Table 2. The following conclusions may be arrived at from a critical study of these data:

1. The effect of the holding energy, and so of pore size, is limited to a small rise in pH and a decrease in SiO<sub>2</sub> concentration as the equivalent diameter decreases.

These variations are easily observable when one considers the mean values for each pF in all the profiles developed over the same material (Fig. 1).

The interpretation of these results is very difficult. In the first place, the low pH values (water from pores between 3 and 10  $\mu\text{m}$ ) are not accompanied by a reduced cation content, so that it would seem necessary to attribute them to the effect of the biological activity, which takes place chiefly in medium or coarse pores: the liberation of CO<sub>2</sub> and perhaps of organic acids would be responsible for these low pH values. A similar interpretation is given by Samoylova & Demkin (1976) for the differences in composition of the soil solution extracted at 5 and 10 atm.

Secondly, in the soils analysed we find that the pH<sub>4</sub>SiO<sub>4</sub> value rises with pF (Fig. 1), which should favour the formation of SiO<sub>2</sub>-poor minerals such as halloysite and kaolinite in the pores of least diameter. Nevertheless, we consider that these results are insufficient to establish beyond doubt a difference between the geochemical processes taking place in pores of different sizes, since the data from water retained in 0.2-10  $\mu\text{m}$  pores can probably not be extrapolated to macropores (> 30  $\mu\text{m}$ ) or to hygroscopic porosities (<0.2  $\mu\text{m}$ ).

2. Where the various horizons of a single profile are concerned, such mutual differences as are observed are of little significance.

We need only mention that the rise in pH and the fall in silica concentration with rising pF are more marked in the horizons rich in organic matter. In any case, these differences are not so great as to change the mineral in equilibrium with the soil solution.

It may therefore be concluded that in the samples analysed neither the quantity nor the type of organic matter greatly affect the equilibria defining the inorganic composition of the soil solution.

3. The most clearly observable effect is that of the parent material. When the data of Table 2 are represented in the stability diagrams proposed by different authors (Garrels & Christ, 1965; Tardy, 1971; Tan et al., 1973; Rai & Lindsay, 1975; etc.) it is found that in all the systems analysed the mineral in equilibrium is kaolinite. By way of an example, we have represented the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-H<sub>2</sub>O system using the diagram proposed by Bolt & Bruggenwert (1976) (Fig. 2).

It may be seen that, even though all the points obtained are within the stability field of the 1:1 clay minerals, there is a different zoning for each parent material, generally agreeing with the mineralogical data obtained for the soils developed over these materials. Thus in the case of the gabbros and amphibolites we find that, even though single-layer silicates are the most abundant minerals in the weathering profiles of both materials, in the gabbros gibbsite is frequent whilst in the amphibolites there is a greater tendency to produce smectite-type minerals in poorly drained areas (Macias et al., 1977). Both associations are easily explained from the data displayed in the diagram of Fig. 3. Similar results were obtained in a study of water from streams flowing through the same types of rock (Garcia Paz et al., 1977).

TABLE 2. Analytical data of the soil solution in the profiles studied (concns. in ppm)

Sample	Horizon	pF	pH	Si	Ca	Mg	Na	K	Al
Gabbros									
No. 1	1328 Aul	3.0	6.95	1.45	1.9	1.9	16.4	10.1	n.d.
No. 2		3.5	7.05	1.15	1.3	2.6	14.5	6.3	0.05
No. 3		4.2	7.25	0.90	1.0	1.6	14.5	11.4	n.d.
No. 4	1328 Au2	3.0	6.10	1.15	1.5	2.6	23.2	6.8	0.60
No. 5		3.5	6.20	0.90	1.8	2.5	20.6	6.9	0.15
No. 6		4.2	6.70	1.05	0.3	1.8	18.3	6.3	0.40
No. 7	1328 2B	3.0	6.70	1.05	0.4	1.0	18.2	4.0	n.d.
No. 8		3.5	6.90	0.75	0.2	0.8	15.0	0.8	0.10
No. 9		4.2	6.75	0.90	2.6	1.4	34.8	4.7	0.25
No. 10	1330 Au1	3.0	6.90	1.05	1.5	2.6	13.6	8.4	0.15
No. 11		3.5	7.10	0.80	1.5	2.9	12.4	6.5	0.05
No. 12		4.2	7.20	0.65	0.9	2.3	13.6	15.5	0.05
No. 13	1330 Au2	3.0	6.10	0.80	0.6	1.2	8.8	9.5	0.10
No. 14		3.5	6.85	0.65	0.6	2.1	8.5	8.8	0.05
No. 15		4.2	7.00	0.55	n.d.	1.6	n.d.	8.1	0.05
Amphibolites									
No. 16	677 A	3.0	7.05	1.20	5.6	2.4	13.3	6.0	n.d.
No. 17		3.5	7.06	1.10	5.0	1.6	7.9	2.0	0.05
No. 18		4.2	7.15	0.95	5.2	1.9	14.5	10.0	n.d.
No. 19	677 2B	3.0	6.65	1.50	3.6	1.8	11.2	2.5	0.15
No. 20		3.5	7.03	1.35	3.6	1.4	7.0	2.0	0.05
No. 21		4.2	7.50	1.15	3.6	1.5	8.5	2.0	0.10
No. 22	1271 A	3.0	6.89	1.50	3.6	1.6	13.3	3.5	0.15
No. 23		3.5	7.14	1.45	3.6	2.2	16.8	3.5	0.15
No. 24		4.2	7.35	1.00	4.2	2.2	n.d.	3.5	0.10
No. 25	1271 B	3.0	6.59	1.25	4.0	1.7	n.d.	3.5	0.30
No. 26		3.5	6.80	1.15	3.8	1.4	8.1	2.0	0.10
No. 27		4.2	7.12	1.40	3.6	1.6	n.d.	3.5	0.10
Mica-schists									
No. 28	1433 Au1	3.0	6.90	1.50	4.0	10.0	108.0	16.0	0.10
No. 29		3.5	6.90	0.65	2.0	6.0	100.0	14.0	0.10
No. 30		4.2	7.05	0.55	n.d.	4.8	54.0	10.8	0.10
No. 31	1433 Au3	3.0	6.70	1.10	2.0	6.0	54.0	1.2	0.15
No. 32		3.5	6.65	0.70	3.0	4.0	50.8	0.4	0.10
No. 33		4.2	6.75	0.95	1.0	5.0	54.8	1.5	n.d.
No. 34	1449 A	3.0	6.80	3.65	n.d.	n.d.	160.0	40.0	0.15
No. 35		3.5	7.00	2.05	n.d.	n.d.	152.0	32.0	0.10
No. 36		4.2	7.00	1.60	n.d.	n.d.	160.0	44.0	n.d.
No. 37	1449 B2	3.0	7.10	1.40	6.0	4.0	52.0	13.0	0.15
No. 38		3.5	7.25	3.30	6.0	4.0	54.0	13.4	0.15
No. 39		4.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
No. 40	1449 B3	3.0	6.50	1.70	3.8	4.4	49.6	11.9	0.10
No. 41		3.5	6.95	1.40	6.7	3.5	42.5	11.9	0.15
No. 42		4.2	6.75	1.60	2.8	3.3	48.8	11.3	n.d.
Granites									
No. 43	1284 A	3.0	5.00	1.90	4.0	9.0	32.4	2.8	0.60
No. 44		3.5	6.30	1.55	4.0	10.0	52.0	2.4	0.15
No. 45		4.2	6.70	1.70	4.0	6.0	56.0	4.6	0.15
No. 46	1233 A	3.0	6.50	3.20	3.0	2.6	20.0	3.6	0.15
No. 47		3.5	6.50	2.30	1.0	1.6	18.8	3.4	0.10
No. 48		4.2	n.d.	1.80	n.d.	n.d.	n.d.	n.d.	n.d.
No. 49	1233 2A	3.0	6.10	1.40	2.0	6.4	n.d.	n.d.	0.15
No. 50		3.5	6.30	1.00	4.0	3.0	n.d.	n.d.	0.10
No. 51		4.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

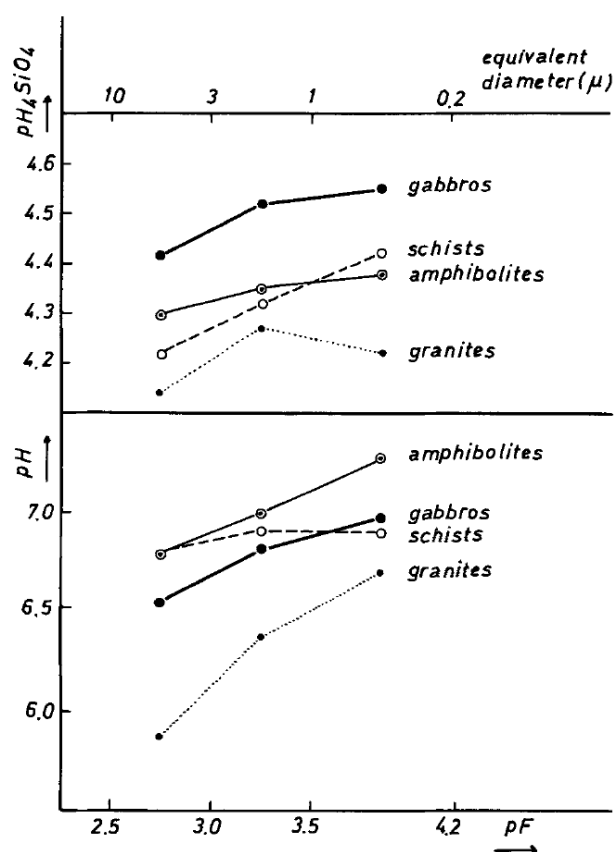


FIG. 1. Variation of  $\text{pH}_4\text{SiO}_4$  and pH of soil solution against pF (mean values for each parent material)

## CONTRIBUTIONS TO THE STUDY OF WEATHERING PROCESSES IN GALICIA

In Fig. 2 it may be seen that there are very few points which reach or approach quartz saturation (samples nos. 34, 38 and 46). Thus it may be held that there is a predominant tendency towards the formation of silica-poor minerals. This tendency is reflected on using the diagram proposed by Tan et al. (1973) for the relationship between kaolinite and gibbsite; a large number of points (nos. 12, 14, 15, 29, 30 and 32) are situated relatively close to the stability field of gibbsite (Fig. 3).

Nevertheless, in the clay fraction of Galician soils there are also found illite-type minerals more or less degraded to vermiculite. According to the results obtained in the analyses of soil solution, and other similar data from river and stream water and lysimetric water (Garcia Paz et al., 1977), these 2:1 minerals should not be stable in the present pedogenetic conditions, and should therefore evolve towards 1:1 phyllosilicates. These results agree with mineralogical analyses of the clay fraction of Galician soils, according to which the principal minerals are: illites, usually appreciably degraded to vermiculite, 1:1 clay minerals (kaolinites, more or less ordered, and halloysites which are generally little hydrated) and, to a much smaller extent, gibbsite. Smectite-type minerals are very rare and limited to particular topographical locations. There are, besides, fairly abundant Fe- and Al-rich amorphous components (Macias et al., 1977).

The question now posed is whether the formation of minerals such as kaolinite, halloysite and gibbsite in Galician soils should be attributed to Tertiary or Pleistocene paleoclimates, as has been suggested for several European soils (Wilson & Tait, 1977; Wilke & Schwertmann, 1977), or whether these minerals are in equilibrium under the present pedogenic conditions, so that the attainment of this state of weathering is no

more than a question of time, variable for each material and 'aggression system' (Hénin et al., 1968).

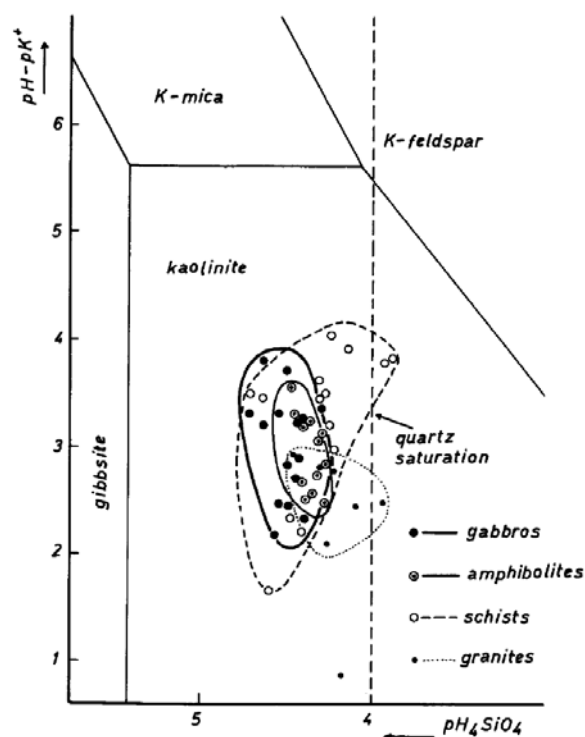


FIG. 2. Representation of soil solution data in the stability diagram for the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$  system according to Bolt & Bruggenwert (1976)

The data available to us are still insufficient to decide this problem in Galicia. Moreover, the possible action of organic matter is not known (and has not been taken into account in the stability diagrams). Evidently, organic matter might 'sequester' a high proportion of Al, thus blocking its evolution towards crystalline forms. Such a sequestration process might explain the high proportion of non-crystalline components that form part of the colloidal fraction of Galician soils.

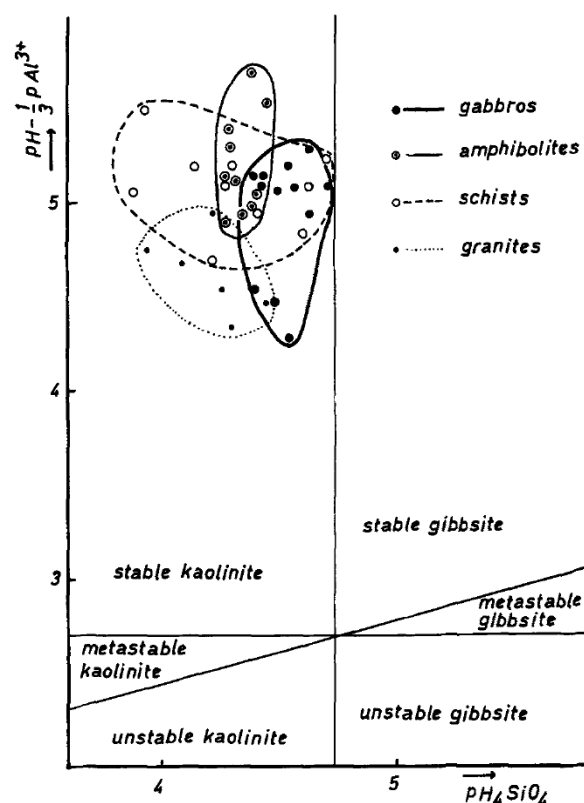


FIG. 3. Representation of soil solution data in the diagram for the relationship between kaolinite and gibbsite in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$  system according to Tan et al. (1973)

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**RESUMEN:** Se realiza un estudio de la composición de la solución del suelo extraída por compresión a diferentes valores de pF como medio de conocer la dirección de los procesos de alteración y neoformación en diversos horizontes de suelos de Galicia, utilizando diagramas de estabilidad de los minerales de la arcilla.

Los resultados más significativos son los siguientes: En todos los casos estudiados el mineral en equilibrio con la solución del suelo es un filosilicato 1:1. La solución extraída a valores crecientes de pF, que corresponden a tamaños de poros más pequeños, presenta valores de pH más altos y disminución de la concentración de sílice. No se aprecian diferencias significativas en cuanto al mineral estable en los diferentes horizontes de un mismo perfil. Para cada material original se aprecia una diferente zonación en los diagramas de estabilidad. Las predicciones de los diagramas de estabilidad están generalmente de acuerdo con los datos mineralógicos de las arcillas de los horizontes correspondientes.

Finalmente se realizan unas breves consideraciones sobre los procesos de alteración en Galicia.

**KURZREFERAT:** Es wurde die Zusammensetzung der Bodenlösung verschiedener Hübel Horizonte von Galicia-Böden untersucht, um Stabilitätsdiagramme von Tonmineralen Einblick in den Verlauf der Verwitterungsprozesse und der Neubildung zu gewinnen. Die Bodenlösung wurde durch Kompression bei verschiedenen pF-Werten extrahiert.

Die bemerkenswertesten Ergebnisse sind: Bei allen untersuchten Proben ist das sich im Gleichgewicht mit der Bodenlösung befindliche Mineral ein 1:1 Phyllosilikat. Mit steigendem pF für die extrahierte Bodenlösung, gleichbedeutend mit geringerer Porengröße, steigt der pH-Wert und fällt die Siliziumkonzentration. Das stabile Mineral verändert sich nicht wesentlich innerhalb der verschiedenen Horizonte ein und desselben Profils. Jedes Ausgangsmaterial gibt eine unterschiedliche Zonierung in den Stabilitätsdiagrammen. Die aus den Stabilitätsdiagrammen zu ziehenden Schlüsse sind in allgemeiner Übereinstimmung mit den mineralogischen Daten der Tone von den betreffenden Horizonten.

Abschließend werden die Verwitterungsprozesse der Böden in Galicia kurz kommentiert.

**RÉSUMÉ:** Dans le but de connaître la direction des processus d'altération et de néoformation dans certains sols de la Galice on étudie la composition de la solution du sol à des pF différentes.

Les résultats plus significatifs peuvent se résumer : Le minéral en équilibre avec la solution du sol est dans tous les cas étudiés un phyllosilicate 1:1. On trouve un pH plus élevé et une diminution de la teneur en silice pour la solution extraite à des valeurs de pF croissantes, qui correspond à des grandeurs de pore plus petites. On ne peut pas apprécier des différences significatives à fin d'établir le minéral stable dans les divers horizons d'un profil. Pour chaque matériel original on constate une différente zonation dans les diagrammes de stabilité. Les prédictions des diagrammes de stabilité sont d'accord vis-à-vis des données minéralogiques des argiles des horizons correspondants.

Enfin on fait quelques brèves considérations sur les processus d'altération en Galicie.